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THE KINETICS OF THE REDUCTION OF FERRIC OXIDE.

By KIMIO KAWAKITA.

It has been admitted that such a solid reaction as the reaction in question is an autocatalytic process. As far as the mechanism of the process is concerned, there are many theories¹⁻¹²⁾ proposed, none of which is decisive. In these theories the formation of the reaction-nuclei has been commonly presumed and the rate of nuclei formation or propagation has been regarded as the rate-determining step of the solid reaction.

Since the reaction velocity of this kind¹³⁾ has been measured by the flow method, it cannot be denied that the accuracy of the measurement is doubtful. Therefore, by measuring the rate of reduction of ferric oxide by hydrogen statically, the author intended to elucidate the mechanism of the autocatalytic process particular to a solid reaction.

Experimental.

The reaction vessel made of quartz was 58.2 c.c. in capacity and it was heated by means of an electric furnace. Much attention was paid to lessen the dead space within the apparatus. 16.5 g. of the ferric oxide prepared by denitrating ferric nitrate of Merck at about 900°C. was used as a catalyst. The hydrogen obtained from a commercial bomb was purified for use.

In the measurement of the rate of reaction, water, the reaction product, was removed by cooling and the decrease in the pressure of hydrogen with the lapse of time was observed statically. After an experiment dried air was intro-

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13) R. N. Pease and H. S. Taylor, *J. Am. Chem. Soc.*, 43, 2179 (1921); 44, 1635 (1922); A. F. Benton and P. H. Emmett, *ibid.*, 48, 632 (1926).

duced at the reaction temperature into the reaction vessel, which was left to stand for more than 24 hours, and then the next experiment was carried out. The preliminary experiments proved that the reaction was approximately reproducible in that way.

Results.

In the temperature range, 200—500°C., the reaction is autocatalytic and its velocity reaches a maximum after a certain lapse of time.

In connection with these facts the author will propose a velocity equation and describe the experimental results on the influences of temperature and pressure on the velocity with some theoretical considerations.

[I] Velocity equation.

The velocity can be expressed from the results of various experiments as follows:

$$\frac{dx}{dt} = kx^n(a-x), \quad (1)$$

where x is the amount of hydrogen reacted; a is the initial concentration of hydrogen; k and n are constants. The equation proved to be applicable to the experimental results over a wide temperature range.

The exponential factor n in equation (1) can be calculated thus: if we take the differential coefficient of the right side of equation (1) to be zero, we obtain the following equation as the maximum condition of equation (1):

$$nx^{n-1}(a-x) - x^n = 0. \quad (2)$$

As $x \neq 0$ during the course of the reaction, this becomes

$$an - (n+1)x = 0. \quad (3)$$

Hence,

$$x = \frac{an}{n+1}. \quad (4)$$

In this way, if the value of x at the maximum velocity is experimentally obtained, n is calculated from equation (4). On the contrary, if n is obtained, x at the maximum velocity will be readily calculated.

[II] Influence of temperature on the reaction velocity.

In the temperature range, 265—600°C., the influence of temperature on the reaction velocity was examined. The results obtained are shown in Fig. 1.

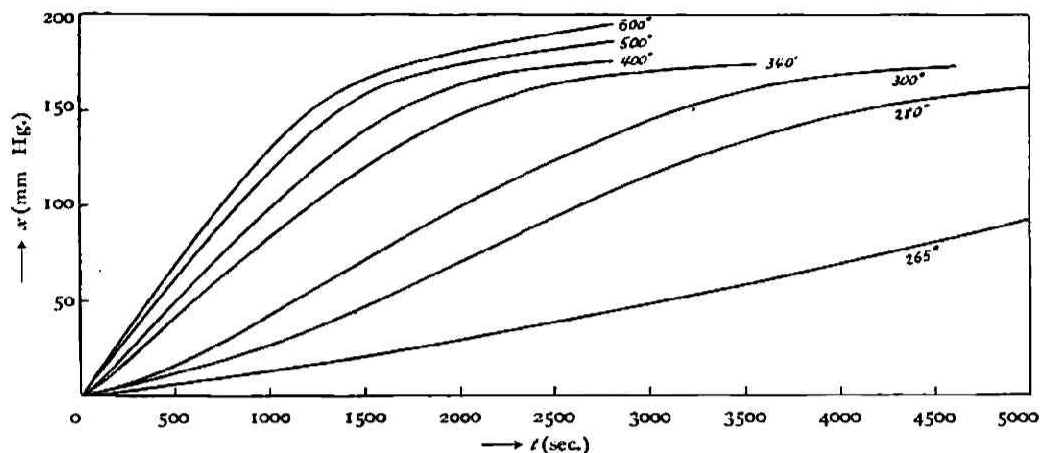


Fig. 1.

In this figure x denotes the pressure decrease (mm. Hg.); the curves are, from up to down, of the experiments carried out at 600, 500, 400, 340, 300, 280, and 265°C. It is evident that the lower the temperature is the more remarkably the autocatalytic nature of the reaction presents itself and that it shows a tendency to disappear with the rise of temperature.

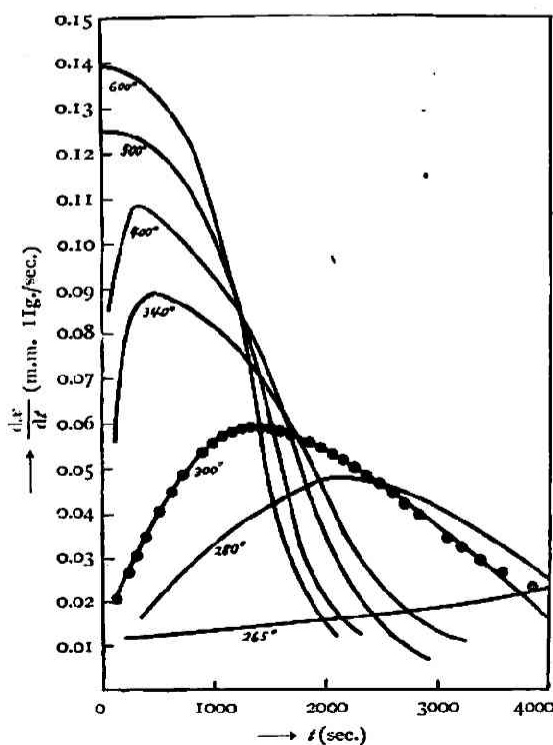


Fig. 2.

The relation between the reaction velocity $\frac{dx}{dt}$ and time t is graphically shown in Fig. 2.

This figure shows that the maximum of the velocity appears below 400°C. and that the lower the temperature is the more strikingly the position of the maximum shifts towards longer duration of time t . In the figure what are marked with black points are the theoretical values calculated from the velocity equation proposed by the author and all the curves give the experimental results.

The relation between n and k in the reaction velocity equation $\frac{dx}{dt} = kx^n(a-x)$, which was obtained from these results, is given in Table I.

Table I.

Reaction Temp. °C.	α (mm. Hg.)	$\left(\frac{dx}{dt}\right)_{\max.}$	Value of x at $\left(\frac{dx}{dt}\right)_{\max.}$	Percentage of the Reaction at $\left(\frac{dx}{dt}\right)_{\max.}$	n	k
265	206.7	0.0256	103.4	50	1	0.0000024
280	198.5	0.0480	75.5	38	0.61	0.000027
300	200.6	0.0600	66.8	33	0.50	0.000054
340	204.0	0.0892	39.0	19	0.24	0.000233
400	201.2	0.1085	30.5	15	0.18	0.000381

The above-described experimental results enable us to understand the following :

1) The higher the temperature is, the larger $\left(\frac{dx}{dt}\right)_{\max.}$ is, and, besides, the earlier it appears.

2) The lower the temperature is, the larger the value of x at $\left(\frac{dx}{dt}\right)_{\max.}$ is, e.g. at 265°C., $\left(\frac{dx}{dt}\right)_{\max.}$ appears when a half amount of the reaction has been completed and the higher the temperature is, it appears the earlier.

3) At both 500 and 600°C., the maximum of the reaction velocity disappears and the reaction velocity comes to be nearly of the first order type.

4) The lower the temperature is, the larger the value of n is, and it is 1 at 265°C. The value of k is the reverse.

In short, the relation between n and k is thus : when n is small, k is large, and vice versa.

From the results shown in Fig. 1 it is observed that the apparent heat of activation calculated is 18—26 kcal./g. mol. in the neighbourhood of 300°C. and that the higher the temperature is the lower the heat of activation is.

[III] Influence of pressure on the reaction velocity.

A series of experiments were carried out under varied initial pressures at 310°C. The results obtained are shown in Fig. 3 and the relation between the reaction velocity and time in Fig. 4.

In Fig. 3 and 4, curves I, II, and III are the cases of the initial pressures 629.0, 382.0, and 200.0 mm. Hg. respectively. As seen in this figure, the higher the initial pressure is, the larger $\left(\frac{dx}{dt}\right)_{\max.}$ is and the longer time its appearance needs. The values of x at $\left(\frac{dx}{dt}\right)_{\max.}$ are 181, 114, and 60 mm. Hg. with respect to curves I, II, and III respectively. And the value of n for the above three experiments calculated from equation (4) is approximately 0.4. Each of these

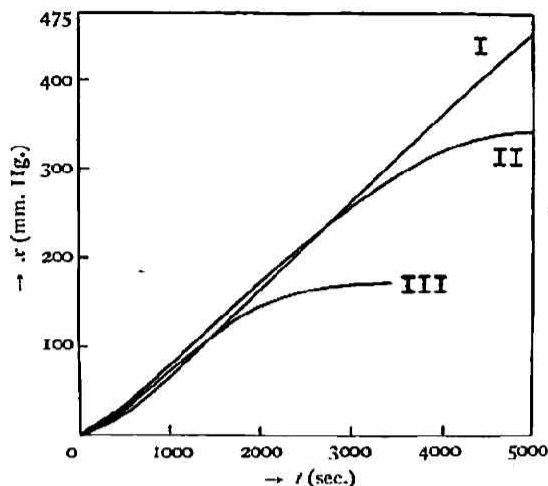


Fig. 3

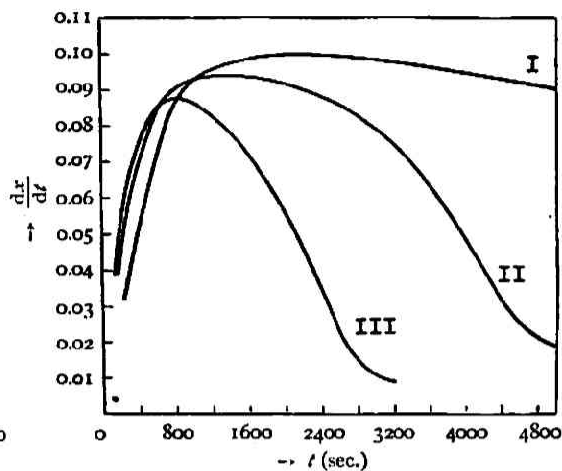


Fig. 4

experiments shows that the reaction velocity reaches a maximum at about 30% of the total amount.

Consideration of the experimental results.

The kinetics of the reaction demands a consideration of the following factors:

- 1) The adsorption velocity of the gaseous molecule by the solid surface;
- 2) The rate of diffusion of the gaseous molecule into the inner surface of solid;
- 3) The rate of reduction of ferric oxide at the inner surface.

Of these three factors, (1) can be neglected because this process is considerably rapid and also because it is presumably not autocatalytic though it should be measured. Such is also the case with (2). In such a case as (2) the velocity is generally measurable in the case when the gaseous molecule reacts on the solid substrate by passing through either a surface film or grain boundaries which would retard the reaction. In the present case, however, any surface film to retard the reaction is considered absent, so that (2) is negligible too. Thus (3) remains to be the sole factor, namely, the reaction velocity measured is considered to be the velocity of the true surface reaction. The experimental results obtained supports the established theory that the reaction takes place at the interface between the solid substrate and the reaction product. At the start of the reaction the nuclei form on the surfaces of solid particles, and then around them the reaction interface is extended. It is, therefore, inferred that the following factors determine the reaction velocity:

- (a) The reaction-nuclei formation ;
- (b) The rate of the propagation of nuclei ;
- (c) The shape and size of the solid particles of a catalyst.

The factor (c) is regarded as nearly constant in this experiment, so that the other two may work simultaneously as the rate-determining step.

As to the velocity equation $\frac{dx}{dt} = kx^n(a-x)$, it goes without saying that x^n of this equation is a factor having a relation to the condition of the surface, surface area, etc., n involving a sort of topochemical factors and taking different values according to the number of nuclei, the nuclei formation, or the condition of the propagation of nuclei.

Let us consider some values of n .

i) $n=0$. This is the case where there are a great number of the reaction nuclei formed at the start of the reaction at high temperatures. In this case, the reaction is of the first order type, thus :

$$\frac{dx}{dt} = k(a-x). \quad (5)$$

For instance, the experiments carried out at 500 and 600°C. (see Fig. 2) somewhat belong to this case.

ii) $n=1$. This is the case where the reaction-nuclei seem very small in number at the start of the reaction. The velocity is expressed by

$$\frac{dx}{dt} = kx(a-x), \quad (6)$$

and its maximum appears when $x = \frac{a}{2}$. The experiment carried out at 265°C. belongs to this case. The velocity reaches a maximum at a half of the initial pressure.

iii) $0 < n < 1$. This is the ordinary case. Suppose the reaction to propagate from one nucleus in a spherical form and represent the radius of the sphere by r , and we shall have $n = \frac{2}{3}$, because the surface area and x are proportional to r^2 and r^3 respectively. Hence, the velocity equation is expressed by

$$\frac{dx}{dt} = kx^{\frac{2}{3}}(a-x). \quad (7)$$

If the nuclei propagate in different ways, n will be various fractional numbers. In the experiments carried out at 280—400°C. the value of n was 0.61—0.18 ; the experiment at 280°C. is approximately the case with equation (7).

Thus, it is understood that n is a constant involving a kind of topochemical factors and is varied by temperature. Variation in n with the change of tem-

perature means that the number of the nuclei or the condition of the nuclei formation is affected by temperature. But whatever the case may be, what first begins to react is considered to be very unstable molecules and at the same time the most highly active spot. This is a consideration similar to those of Taylor¹⁴⁾ Schwab and Pietsch¹⁵⁾ concerning a solid catalyst in the gaseous reaction. Such unstable molecules must possess the lowest energy of activation of the chemical reaction. Consequently, their rate is the highest, so that the reaction is started by them.

Once the nuclei are formed, the neighbouring molecules of the substrate which have not reacted will be so much activated as to react. The reaction, therefore, occurs solely where the substrate is in contact with the reaction product. This consideration is in agreement with the fact that a solid reaction is autocatalytic.

Summary.

(1) The velocity of the reduction of ferric oxide by hydrogen has been statically measured in the temperature range, 200—600°C.

(2) The velocity equation:

$$\frac{dx}{dt} = kx^n(a-x)$$

has been proposed

(3) It has been pointed out that n in the equation is a constant to be varied by temperature and that it has a topochemical meaning.

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